

# SYNTHESIS AND CHARACTERIZATION OF CATALYSTS CONTAINING MOLYBDENUM AND TUNGSTEN AND THEIR APPLICATION IN PARAFFIN ISOMERIZATION

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## ABSTRACT

*The development of new catalysts for normal alkanes isomerization reveals a big importance. Three series of catalysts were prepared by using sol-gel method, using different metal concentration and in two different pH (acid and basic). The first series contains molybdenum, the second contains tungsten and the third contains the two metals (molybdenum and tungsten). The catalysts were characterized by several techniques; the obtained results show that the catalysts prepared in basic pH have a surfaces areas and porous volumes higher than those prepared in acid pH. In order to evaluate the catalytic performances of prepared catalysts, we carried out the catalytic tests with light naphtha (C5, C6) isomerization. The obtained results show that the best conversions are obtained with catalysts prepared into pH basic. The octane numbers of the obtained products (isomerate) are high compared to naphtha. The addition of the obtained products (isomerate) into the pool gasoline allows on the one hand, to obtain gasolines with high octane numbers which respect the environmental standards, and on the other hand, the possibility of developing the light fractions (C5 - C6) resulting from the crude oil distillation unit and condensed split distillation.*

**KEYWORDS:** Isomerization, Pollution, Catalyst, Molybdenum, Tungsten

## I. INTRODUCTION

The deterioration of the natural environment by an increasing pollution due to vehicles emissions has been subject to increasingly severe environmental regulations aiming in reducing vehicles emissions by introducing new specifications for fuels.

Among these specifications the total elimination of lead additions to fuels, the reduction of aromatic, olefins and sulphur content, and the increase of octane number.

Environmental reasons are motivating the production of transportation fuels with increase amount of high octane number branched alkanes [1]. These compounds are made by alkylation and by isomerization of straight-chain alkanes. The drawback of these two processes is that they employ harmful and potentially polluting catalysts, such as H<sub>2</sub>SO<sub>4</sub>, and HF [2, 3].

The isomerization for normal paraffin to isoparaffin is regarded as one of the important technologies for RON improvement in oil refining [4, 5, 6] and it is one of the largely used petrochemical processes. It is well known that low temperatures are preferred for alkane isomerization processes because the equilibria favors branched (high-octane-number) products, thus in order to achieve maximum isomer yields, the isomerization of n-paraffins must be carried out at the lowest possible temperatures over highly efficient catalysts [7, 8, 9, 10].

Industrially the catalyst used for alkane's isomerisation is chlorinated platinum-alumina; this catalyst is very sensitive to the poisons and present corrosion problems [11], of this fact the development of new isomerization catalysts reveals a big importance and extensive research has been done in the search for such catalysts, in this context H. Al-Kandari and al [12] have studied the isomerization reaction of n-hexane using molybdenum trioxide partially reduced and deposited on TiO<sub>2</sub>, depending

on the weight of molybdenum. These authors reported that at temperature of 623 °C and hydrogen flow rate of 3 to 15 bars the conversion is about 80% with a selectivity of 90% in mono- and di-branched isomers.

Holl and Al [13] showed that the catalysts  $\text{MoO}_3 / \text{Al}_2\text{O}_3$ , in which the molybdenum is reduced to the metallic state (at 950 °C) catalyzes the isomerization reaction of hexanes.

Hino and Arata [14] have reported that the catalysts  $\text{Mo/ZnO}_2$  and  $\text{W/ZnO}_2$  prepared by impregnation and calcined between 800 °C and 900 °C are active in the isomerization reactions of n-pentane and n-hexane with a significant participation of the cracking reactions.

Inglesia and Coll [15, 16] show that the tungsten carbides treated with oxygen are highly selective for the isomerization of hexanes and heptanes. They offer a classical bifunctional mechanism,

The sol-gel is one of the catalysts preparation methods; this way of synthesis is a homogeneous process resulting in a continuous transformation of a solution into hydrated solid precursor (hydrogel) [17, 18, 19]. The gelation route (sol-gel process) has several promising advantages over the conventional techniques. It offers better control of the texture, composition, homogeneity and structural properties of the final solids [20, 21, 22, 23, 24, 25].

Our work in this article is to develop new catalysts with molybdenum and tungsten for the alkanes' isomerisation reaction using the sol-gel method.

We developed three series of catalysts, the first series with molybdenum ( $\text{MoO}_3 / \text{Al}_2\text{O}_3 - \text{SiO}_2$ ), the second with tungsten ( $\text{WO}_3 / \text{Al}_2\text{O}_3 - \text{SiO}_2$ ) and the third with the two metals (Mo and W) ( $\text{MoO}_3 - \text{WO}_3 / \text{Al}_2\text{O}_3 - \text{SiO}_2$ ).

Our first objective in this work is to study the metal adding effect (Mo, W) on the catalysts characteristics (surface area, porous volume) and on the alkanes' isomerisation.

The second objective is to study the pH effect on the catalysts characteristics; we prepared catalysts with pH 4.55 and catalysts with pH 7.

The third objective is to study the effect of the metal's nature on the catalysts characteristics; we prepared catalysts with molybdenum, with tungsten and with the two metals (Mo and W).

The obtained catalysts were tested on the isomerisation reaction of light naphtha (C5, C6) resulting from the atmospheric crude oil distillation.

The obtained products (isomerisats) were analyzed and the obtained results shows a considerable increase of octane number and isoparaffins content compared to naphtha, these results confirm the isomerisation properties of the prepared catalysts.

## II. EXPERIMENTAL

### 2.1. Catalysts Preparation

By using sol-gel method three series of catalysts were prepared, the first series contains molybdenum ( $\text{MoO}_3 / \text{Al}_2\text{O}_3 - \text{SiO}_2$ ), the second contains tungsten ( $\text{WO}_3 / \text{Al}_2\text{O}_3 - \text{SiO}_2$ ) and the third contains the two metals (molybdenum and tungsten) ( $\text{MoO}_3 - \text{WO}_3 / \text{Al}_2\text{O}_3 - \text{SiO}_2$ ).

The catalysts were synthesised with different metal concentration (Table 1 and 2) and in two different pH, one acid (pH = 4.5) and the other basic (pH = 10.5).

For the first series of preparation we prepared the acidic gel by mixing the required amounts of aluminum sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ ) with ammonium heptamolybdate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$  preliminarily acidified by nitric acid. To the obtained sol, under vigorous stirring, an aqueous solution of sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) with  $\text{Na}_2\text{O} / \text{SiO}_2 = 2$  was added. The obtained gel have a pH = 4.5. Whereas to obtain a basic gel an aluminum sulphate and ammonium heptamolybdate were added to the sodium silicate solution, the obtained gel have a pH = 10.5.

Then the obtained sol was activated in thermostat at temperature ranging between 60 ÷ 80 °C. This operation consists to exchange undesirable ions, such as  $\text{Na}^+$  by ions ammonium, by treating the prepared gel with ammonia sulfate  $(\text{NH}_4)_2\text{SO}_4$  at 20 g/l. After the catalyst were washed with water at temperature ranging between 60 ÷ 80 °C. The complete elimination of undesirable ions was tested with  $\text{AgNO}_3$  and  $\text{BaCl}_2$  solutions. Finally the catalysts were dried at 120 °C for 6 h and calcined at 700 °C.

For the preparation of series 2 and 3 is the same method with series 1, while in serie 2 the used solution is sodium tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) and in serie 3 the two solutions  $(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  were added.

**Table 1.** Chemical Composition of Catalysts Prepared at pH = 4.5

Catalyst	% $\text{MoO}_3$	% $\text{WO}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$
$(\text{MoO}_3)_{1B}$	4	-	2
$(\text{MoO}_3)_{2B}$	6	-	2
$(\text{MoO}_3)_{3B}$	8	-	2
$(\text{MoO}_3)_{4B}$	12	-	2
$(\text{WO}_3)_{1B}$	-	4	2
$(\text{WO}_3)_{2B}$	-	6	2
$(\text{WO}_3)_{3B}$	-	8	2
$(\text{WO}_3)_{4B}$	-	12	2
$(\text{MoO}_3 - \text{WO}_3)_{1B}$	2	2	2
$(\text{MoO}_3 - \text{WO}_3)_{2B}$	2	6	2
$(\text{MoO}_3 - \text{WO}_3)_{3B}$	6	2	2
$(\text{MoO}_3 - \text{WO}_3)_{4B}$	6	6	2

With:  $(\text{MoO}_3)_{iA}$ :

i = catalyst number

i = 1, 2, 3, 4

A = acid

**Table 2.** Chemical Composition of Catalysts Prepared at pH = 10.5

Catalyst	% $\text{MoO}_3$	% $\text{WO}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$
$(\text{MoO}_3)_{1A}$	4	-	2
$(\text{MoO}_3)_{2A}$	6	-	2
$(\text{MoO}_3)_{3A}$	8	-	2
$(\text{MoO}_3)_{4A}$	12	-	2
$(\text{WO}_3)_{1A}$	-	4	2
$(\text{WO}_3)_{2A}$	-	6	2
$(\text{WO}_3)_{3A}$	-	8	2
$(\text{WO}_3)_{4A}$	-	12	2
$(\text{MoO}_3 - \text{WO}_3)_{1A}$	2	2	2
$(\text{MoO}_3 - \text{WO}_3)_{2A}$	2	6	2
$(\text{MoO}_3 - \text{WO}_3)_{3A}$	6	2	2
$(\text{MoO}_3 - \text{WO}_3)_{4A}$	6	6	2

With:  $(\text{MoO}_3)_{iB}$  :

i = catalyst number

i = 1, 2, 3, 4

B = Basic

## 2.2 Catalysts characterization

### 2.2.1 Infrared spectroscopy

The prepared catalysts were analyzed by infrared spectroscopy, the obtained spectres shows that the spectres takes the same general form and the bands observed are represented in table 3.

Fig. 1 and table 3 gives the infrared specters of catalysts

**Table 3.** Infrared Spectres

Bande d'absorption ( $\text{Cm}^{-1}$ )	Caractérisation
3400 – 3500	Attribute to the hydroxyls O-H
1630 – 1620	Attribute to the water molecule vibration.
1060 – 1050	Attribute to the Si-O-Al and Al-O-OH
795 - 790	Elongation of Si-O
500 – 450	Attribute to the metallic oxides

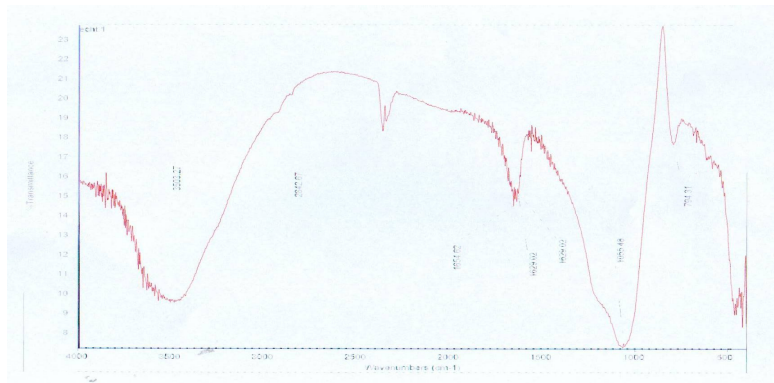


Figure 1. Infrared Spectres

### 2.2.2 Surface area

The surface area was determined by the BET method; we measured the adsorption isotherm of nitrogen at liquid nitrogen temperature using Quantachrome NovaWin2 version 9.0.

Fig. 2 gives the evolution of the surface area of catalysts prepared in acid pH (pH= 4.5) for the three series of catalysts.

Fig. 3 gives the evolution of the surface area of catalysts prepared in basic pH (pH= 10.5) for the three series of catalysts.

From the results, it can be observed that the specific surface area decreased with increasing molybdenum and tungsten loading.

Based on curves of Fig. 2 and Fig. 3 the surface area of serie 3 (catalysts containing Mo and W) are higher than catalysts of serie 2 (catalysts containing w) and serie 1 (catalysts containing Mo)

Fig. 2 and 3 show that the surfaces area obtained in basic pH (pH= 10.5) are higher then obtained in acid pH; this result was explained by I.M.KOLESNIKOV and coll [26, 27] by relative speeds of hydrolysis and condensation reactions during the gelation. In acid pH the speed of condensation is very low compared with hydrolysis reaction, the prepared gel was not very ramified and the resulting oxide will be with low surface area.

The surface area of catalysts is inversely proportional to the metal contained in the catalyst. This fact could be interpreted by the formation of octahedral molybdates species (or tungstates octahedral in the tungsten case) those could block the catalyst pores justifying the reduction in surface area [28, 29].

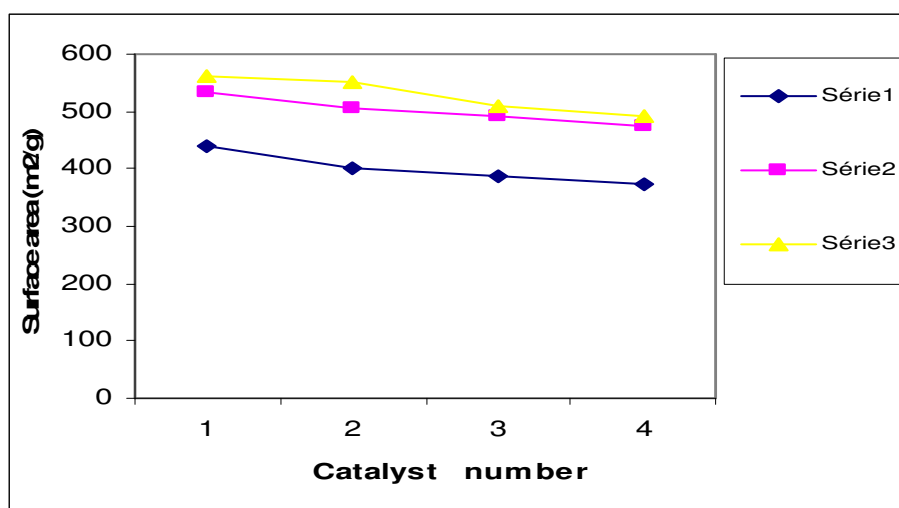


Figure 2. Surfaces area at pH = 4.5

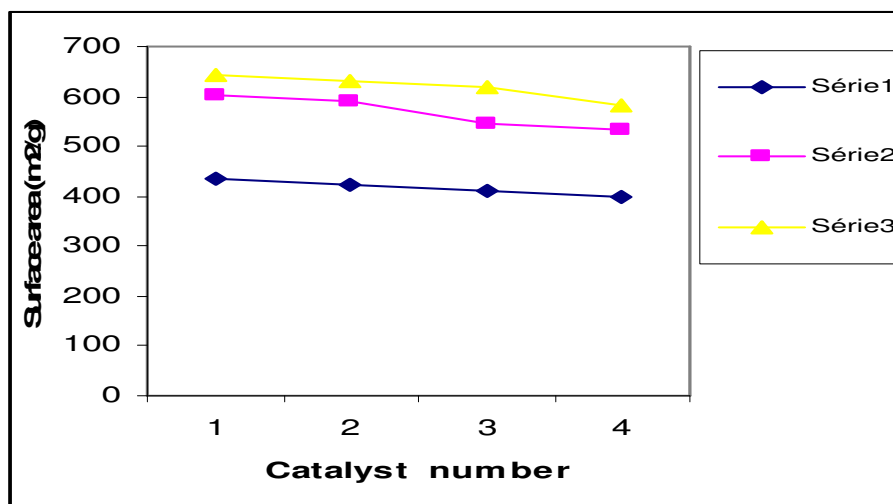


Figure 3. Surfaces area at pH = 10.5

### 2.2.3 Porous volume

Fig. 4 gives the evolution of the porous volume of catalysts prepared in acid pH (pH= 4.5) for the three series of catalysts.

Fig. 5 gives the evolution of the porous volume of catalysts prepared in basic pH (pH= 10.5) for the three series of catalysts.

The results show that the porous volume of catalysts vary with the pH of preparation. The catalysts with pH = 10.5 have a porous volumes higher than those obtained with catalyst at pH = 4.5, this result is related to the micellar organization of colloidal particles during the preparation of sols.

The increasing on the metal content causes a decrease in porous volume, this result is related to the formation of octahedral molybdates (tungstates), which could lead to blocking of micropores [30, 31].

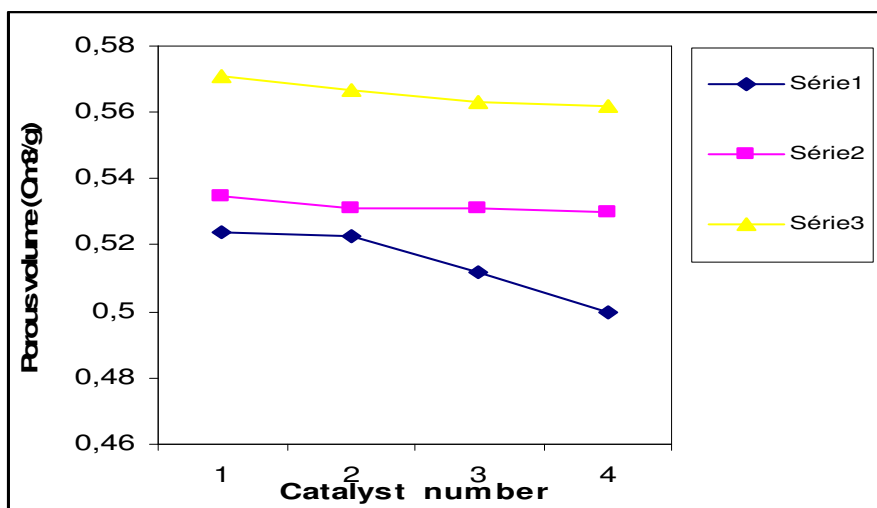


Figure 4. Porous volume at pH = 4.5

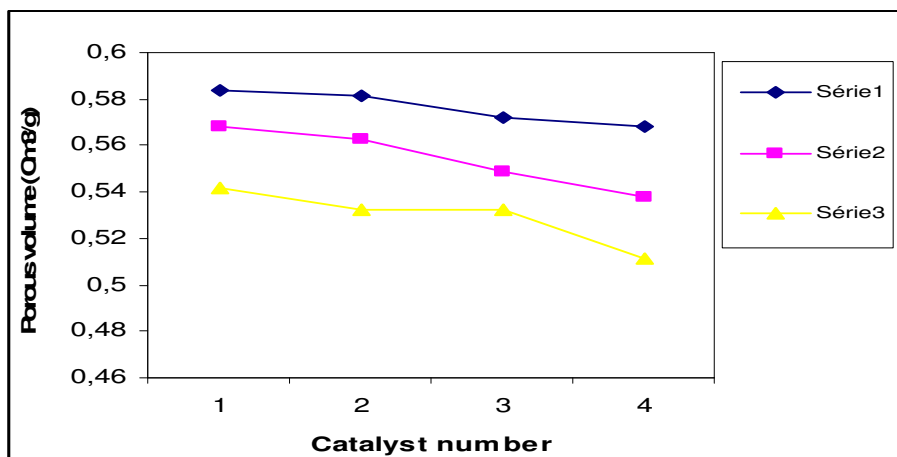


Figure 5. Porous volume at pH = 10.5

### III. CATALYTIC TESTS

In order to evaluate the catalytic performances of prepared catalysts, we have carried out the catalytic tests on the isomerization of light naphtha ( $C_5$ ,  $C_6$ ) obtained by the crude oil distillation unit.

#### 3. 1. Light Naphtha Characteristics

Light naphtha ( $C_5$ ,  $C_6$ ) characteristics are mentioned in table 4 and 5.

Table 4. Naphtha characteristics

Characteristics	Naphtha
Density at 15 °C	0.6496
Vapor tension (KPa)	75
Index of refraction at 20 °C	1.3740
Octane number (NOR)	64
Copper foil corrosion	negative

Table 5. Chromatographic analysis of naphtha

Family	% weight
Normal paraffins	53.390
Iso-paraffins	32.493
Naphtenes	11.298
Aromatic	2.668
Unknown	0.151

#### 3. 2. Operating Conditions

The operating conditions of catalytic tests are mentioned in table 6.

Table 6. Operating Conditions

Parameter	Value
Temperature	250°C
Weight hourly space velocity	2 h <sup>-1</sup>
Hydrogen Pressure	8 atm
Mass of catalyst	2 g
Grains diameter	0.5 mm

The catalytic experiments were performed in a continuous flow fixed-bed quartz reactor, loaded with 2 g of the catalyst, operated under isothermal conditions, and heated by a controlled temperature electrical oven. The naphtha conversion was studied at atmospheric pressure, 250 C, weight hourly space velocity (WHSV) = 2 h<sup>-1</sup>.

### 3. 3. Analyze of obtained products (isomerase) by chromatography

The chromatographic analyses (table 7) of obtained products are realized on chromatograph Hewlett Packard (modèle 6890 N).

**Table7.** Chromatographic Analyses of Obtained Products

Product obtained by Catalyst (isomerase) :	% weight				
	n-paraffins	Iso-paraffins	Naphtene	Aromatic	Unknown
(MoO <sub>3</sub> ) <sub>1A</sub>	42.413	46.139	9.312	1.964	0.172
(MoO <sub>3</sub> ) <sub>2A</sub>	40.893	48.004	9.107	1.846	0.150
(MoO <sub>3</sub> ) <sub>1B</sub>	38.408	53.324	6.505	1.632	0.151
(MoO <sub>3</sub> ) <sub>2B</sub>	36.225	54.193	7.621	1.782	0.179
(WO <sub>3</sub> ) <sub>1A</sub>	39.780	48.193	8.713	2.136	1.178
(WO <sub>3</sub> ) <sub>2A</sub>	37.391	52.723	9.054	1.607	0.161
(WO <sub>3</sub> ) <sub>1B</sub>	36.225	54.193	7.621	1.782	0.179
(WO <sub>3</sub> ) <sub>2B</sub>	33.542	57.593	6.432	1.932	0.501
(Mo-WO <sub>3</sub> ) <sub>1A</sub>	36.912	52.803	8.116	1.993	0.176
(Mo-WO <sub>3</sub> ) <sub>2A</sub>	34.391	57.093	7.661	0.734	0.121
(Mo-WO <sub>3</sub> ) <sub>1B</sub>	34.545	57.493	6.727	1.083	0.152
(Mo-WO <sub>3</sub> ) <sub>2B</sub>	27.891	63.293	6.644	1.559	0.613

### 3. 4 Octane Number Determination of Obtained Products (Isomerisat)

Octane number (table 8) of obtained products (isomerase) was determined by using chromatographic analyses and calculating method of Walsh [32, 33].

**Table 8.** Octane number of isomerase

Product obtained by Catalyst (isomerase)	Octane number (NOR)
(MoO <sub>3</sub> ) <sub>1A</sub>	70
(MoO <sub>3</sub> ) <sub>2A</sub>	71
(MoO <sub>3</sub> ) <sub>1B</sub>	73
(MoO <sub>3</sub> ) <sub>2B</sub>	73
(WO <sub>3</sub> ) <sub>1A</sub>	71
(WO <sub>3</sub> ) <sub>2A</sub>	72
(WO <sub>3</sub> ) <sub>1B</sub>	74
(WO <sub>3</sub> ) <sub>2B</sub>	80
(Mo-WO <sub>3</sub> ) <sub>1A</sub>	73
(Mo-WO <sub>3</sub> ) <sub>2A</sub>	81
(Mo-WO <sub>3</sub> ) <sub>1B</sub>	82
(Mo-WO <sub>3</sub> ) <sub>2B</sub>	83

Chromatographic analysis of obtained products shows a considerable increase of isoparaffins content compared to the naphtha, these results confirms the isomérisantes properties of prepared catalysts.

The obtained products by catalysts prepared in basic pH gave high content of isoparaffins compared to those prepared in acid pH.

The simultaneous presence of molybdenum and tungsten in the catalyst improved the isoparaffins content compared to monometallic catalysts; this result is dependant on the bimetallic character of catalysts and a synergy between two metals for the isomerisation reaction.

The isoparaffins content is higher when increased the metal quantity in the catalyst; thus increased metal function of the catalysts prompts the formation of isomers via a reduction of the diffusion path between two metallic sites. Hence, the possibility that the intermediate species would encounter acid sites and would be cracked during its migration from one metallic site to another is also less [34].

#### IV. CONCLUSIONS

The sol-gel method allow to prepare molybdenum and tungsten catalysts for light naphtha isomerization, the obtained results show that surface area is according to the quantity of metal contained in catalyst. The surface area obtained in basic pH is higher than those obtained in acid pH.

The products obtained (isomérate) by the light naphtha ( $C_5 - C_6$ ) isomerization with the presence of prepared catalysts present isoparaffins contents and octane numbers higher compared to the naphtha.

The addition of obtained products (Isomérate) into the pool gasoline allows on the one hand, to obtain gasolines with high octane numbers, witch respect the international and environmental requirements and on the other hand, the possibility of developing the light fractions ( $C_5 - C_6$ ) resulting from the crude oil distillation unit and condensed split distillation.

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